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Analytic method for lithium hexafluorophosphate

六氟磷酸锂产品分析方法

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Analytic method for lithium hexafluorophosphate

Warning: Lithium hexafluorophosphate will rapidly absorb moisture and hydrolyze, when exposed to humid air, to generate fumes. The fumes are hydrogen fluoride, which is corrosive. The operation for lithium hexafluorophosphate must be carried out, in a glove box (required dew point ≤ -40 °C) or a fume hood. Some of the reagents, which are used in the test, are toxic or corrosive, so be careful when handling them! If they splash on the skin, they shall be washed by water immediately; if they are serious, it shall seek medical treatment immediately.

1 Scope

This standard specifies the identification of lithium hexafluorophosphate products AND the analytical methods of related physical and chemical indicators.

This standard applies to lithium hexafluorophosphate products.

2 Normative references

The following documents are essential to the application of this document. For the dated documents, only the versions with the dates indicated are applicable to this document; for the undated documents, only the latest version (including all the amendments) is applicable to this standard.

GB/T 6283-2008 Chemical products - Determination of water Karl·Fischer method (general method)

GB/T 6682-2008 Water for analytical laboratory use - Specification and test methods

HG/T 3696.1 Inorganic chemicals for industrial use - Preparations of standard and reagent solutions for chemical analysis - Part 1: Preparations of standard volumetric solutions

HG/T 3696.2 Inorganic chemicals for industrial use - Preparations of standard and reagent solutions for chemical analysis - Part 2: Preparations of standard solutions for impurity

HG/T 3696.3 Inorganic chemicals for industrial use - Preparations of standard and reagent solutions for chemical analysis - Part 3: Preparations of reagent solutions

3 Analytical methods

3.1 General provisions

The reagents and water, which are used in this standard, refer to the first-grade pure reagents and the first-grade water, which are specified in GB/T 6682-2008, unless other requirements are specified. For the standard solutions for chemical analysis, standard solutions of impurities, preparations and products, which are used in the test, they shall be prepared in accordance with the provisions of HG/T 3696.1, HG/T 3696.2, HG/T 3696.3, unless other requirements are specified.

3.2 Identification test

3.2.1 Raman spectroscopy

Adjust the power of the light source. After the instrument is stable, take an appropriate amount of specimen. Quickly press it into the sample cell. Put the sample cell on the sample chamber support. Align the light source. Make measurement. The intensity of the absorption peak of the tested sample shall be consistent with the lithium hexafluorophosphate in the spectral library.

3.2.2 X-ray diffraction method

The determination is carried out, according to the operating requirements of the X-ray diffractometer. Adjust the gain of the diffractometer, so that the height of the diffraction peak of the measured crystal plane reaches the maximum value, within the recording range; the angle ranges from 20° to 80°. Determine the plane spacing of the characteristic diffraction peaks AND the intensity of the diffraction peak of the crystal plane, through observation, which shall be consistent with that of the lithium hexafluorophosphate, in the spectral library

3.2.3 Infrared spectroscopy

Grind the sample and liquid paraffin, to make it evenly dispersed. Use the potassium bromide wafer smearing method, to prepare specimen, to determine the absorption peak. It is compared with the hexafluorophosphate in the spectral library, for judgement.

3.3 Determination of cation content

3.3.1 Standard addition method

3.3.1.1 Method summary

The content of each cation in the specimen is determined, by standard addition method, on an inductively coupled plasma optical emission spectrometer (ICP-OES), which has a hydrofluoric acid-resistant sampling system.

state, use water as the blank, to measure the working curve solution. Take the measured cation concentration as the abscissa, AND the corresponding response value as the ordinate, to draw a working curve.

3.3.2.4.3 Determination

Measure the response value of each cation, in the test solution, under the same instrument conditions. Find out the mass concentration (μg/L) of the measured cation, in the specimen solution, on the standard curve.

3.3.2.5 Result calculation

The cation content is calculated in mass fraction w_1; the value is expressed in mg/kg; it is calculated according to formula (2):

$$w_1 = \frac{\rho_x V \times 10^{-3}}{m} \qquad \cdots\cdots (2)$$

Where:

ρ_x - The value of the concentration of each measured cation, in the test solution, which is obtained from the working curve, in micrograms per liter (μg/L);

V - The value of the constant volume of the prepared test solution, in milliliters (mL);

m - The value of the mass of the sample, in grams (g).

Take the arithmetic mean of the parallel determination results as the determination result. The ratio -- of the absolute difference between the two parallel determination results TO the arithmetic mean -- is not more than 30%.

3.4 Determination of anion content

3.4.1 Method summary

The chloride ion and sulfate ion, in lithium hexafluorophosphate, are separated by chromatographic column; detected by conductivity detector. The content of detected anion is calculated by external standard method.

3.4.2 Reagents

3.4.2.1 Water: Deionized water, which has a conductivity (25 °C) not greater than 0.0055 mS/m.

3.4.2.2 Ice water: Add an appropriate amount of ice cubes to the water. Use it, when the water temperature is ≤ 4 °C.

Store it at 4 °C. The validity period is 30 days.

3.5.2 Analytical procedures

3.5.2.1 Preparation of standard turbidity solution

In a series of 50 mL colorimetric tubes, add 0.00 mL, 1.00 mL, 2.00 mL, 4.00 mL, 6.00 mL, 8.00 mL, 10.00 mL of the above diluted chloride standard solution, respectively. Add 2 mL of nitric acid solution, 1 mL of silver nitrate solution. Dilute it to 25 mL. Shake well. Let it stand for 5 min.

3.5.2.2 Determination

Weigh about 5 g of specimen in the glove box, accurate to 0.01 g. Take it out and place it in a polyethylene beaker, which is filled with 15 mL of water. Dissolve and filter it. Transfer the filtrate into a 50 mL colorimetric tube. Add 2 mL of nitric acid solution and 1 mL of silver nitrate solution. Dilute it to 25 mL. Shaken well. Let it stand for 5 min. Use the visual turbidimetry for determination. The turbidity shown is compared with the standard turbidity solution.

3.6 Determination of sulfate content

3.6.1 Method principle

In hydrochloric acid medium, barium ions and sulfate ions form insoluble barium sulfate. When the content of sulfate ions is low, barium sulfate will be in suspension, within a certain period of time, making the solution turbid, which can be determined, by the visual turbidimetry.

3.6.2 Reagents

3.6.2.1 Absolute ethanol.

3.6.2.2 Hydrochloric acid solution: 1 + 1.

3.6.2.3 Barium chloride solution: 250 g/L.

3.6.2.4 Sulfate standard solution: 1 mL solution contains 1.0 μg of sulfate (SO_4). Pipette 10 mL of sulfate standard solution, which is prepared according to HG/T 3696.2. Put it in a 100 mL volumetric flask. Use water to dilute it to the mark. Shake well. Pipette 1 mL into a 100 mL volumetric flask. Use water to dilute it to the mark. Shake well. Store it at 4 °C. The validity period is 30 days.

3.6.3 Analytical procedures

3.6.3.1 Preparation of standard turbidity solution

Pipette 0.00 mL, 5.00 mL, 10.00 mL, 15.00 mL of sulfate standard solution, into a 25 mL colorimetric tube, respectively. Add 0.3 mL of hydrochloric acid solution and 3 mL of absolute ethanol in sequence. Then use water to dilute it to 25 mL. Shake well. Add 2 mL of chlorine barium chloride solution. Shake well.

3.6.3.2 Determination

Weigh about 5 g of the specimen in the glove box, accurate to 0.01 g. Take it out and place it in a polyethylene beaker, which is filled with 15 mL of water. Dissolve and filter it into a 25 mL colorimetric tube. Then treat it, together with the standard turbidity solution at the same time. The turbidity of the solution is compared with that of the standard turbidity solution.

3.7 Determination of moisture

3.7.1 Method principle

Same as Chapter 3 of GB/T 6283-2008.

3.7.2 Instruments and equipment

3.7.2.1 Automatic moisture analyzer: Coulomb coulometric method.

3.7.2.2 Glove box: dew point < -40 °C.

3.7.3 Analytical procedures

The analytical procedure shall be carried out in a glove box. Weigh about 0.5 g of the specimen, accurate to 0.001 g. Put the specimen into the measuring bottle of the automatic moisture analyzer, until it is completely dissolved. Stir evenly. Then measure its moisture.

3.7.4 Result calculation

The mass fraction w_3 of water, expressed in mg/kg, is calculated according to formula (4):

$$w_3 = \frac{m_{H_2O}}{m} \qquad \cdots\cdots (4)$$

Where:

m_{H2O} - The value of the water mass, which is measured by the moisture meter, in micrograms (μg);

m - The value of the mass of the sample, in grams (g).

Take the arithmetic mean of the parallel determination results, as the determination result. The ratio -- of the absolute difference between the two parallel determination the operation.

3.8.5 Result calculation

The insoluble content of dimethyl carbonate (DMC) is calculated in mass fraction w_4; the value is expressed in mg/kg; it is calculated according to formula (5):

$$w_4 = \frac{(m_2 - m_1) \times 10^{-6}}{m} \quad \cdots\cdots (5)$$

Where:

m_1 - The value of the mass of the weighing bottle and the filter membrane, after drying, in the blank test, in grams (g);

m_2 - The value of the mass of the weighing bottle, filter membrane, dimethyl carbonate (DMC) insoluble, after drying, in grams (g);

m - The value of the mass of the sample, in grams (g).

Take the arithmetic mean of the parallel determination results as the determination result. The ratio -- of the absolute difference between the two parallel determination results TO the arithmetic mean -- is not more than 20%.

3.9 Determination of free acid content

3.9.1 Method summary

Use a micro-burette. Use bromothymol blue as an indicator. Use standard titration solution of sodium hydroxide, to titrate the free acid in the specimen.

3.9.2 Reagents

3.9.2.1 Sodium hydroxide standard titration solution: c(NaOH) ≈ 0.01 mol/L. Preparation: Pipette 100 mL of sodium hydroxide standard solution, which is prepared according to HG/T 3696.1. Place it in a 1000 mL volumetric flask. Use carbon dioxide-free water to dilute it to the mark. Shake well.

3.9.2.2 Ice water: Add an appropriate amount of ice cubes to the water. Use it when the water temperature is ≤ 4 °C.

3.9.2.3 Bromothymol blue indicator solution: 1 g/L.

3.9.3 Instruments and equipment

3.9.3.1 Beaker: Polyethylene or other corrosion-resistant material.

3.9.3.2 Micro-burette: The division value is 0.01 mL or 0.02 mL.

3.9.4 Analytical procedures

Weigh about 10 g of the sample by weight loss method, accurate to 0.0002 g. Quickly pour the sample into a beaker, which contains 100 mL of ice water. Shake the beaker, to dissolve the specimen quickly. Add 10 drops of bromothymol blue indicator solution. Use sodium hydroxide standard titration solution, to rapidly titrate it to light blue (no color fading in 10 s), which is the end point. At the end point, the temperature of the solution shall still remain ≤ 4 °C.

At the same time, carry out a blank test. The type and amount of reagents added into the blank test solution is the same as that of the test solution, except that no specimen is added.

3.9.5 Result calculation

The free acid content is calculated in terms of the mass fraction w_5 of hydrofluoric acid (HF); the value is expressed in mg/kg; it is calculated according to formula (6):

$$w_5 = \frac{(V - V_0)cM}{m \times 10^{-3}} \quad \cdots\cdots (6)$$

Where:

V - The value of the volume of the standard titration solution of sodium hydroxide, which is consumed by the titration test solution, in milliliters (mL);

V_0 - The value of the volume of the standard titration solution of sodium hydroxide, which is consumed by titrating the blank test solution, in milliliters (mL);

c - The exact value of the concentration of the standard titration solution of sodium hydroxide, in moles per liter (mol/L);

m - The value of the mass of the sample, in grams (g);

M - The numerical value of the molar mass of hydrofluoric acid (HF), in grams per mole (g/mol) (M = 20.01).

Take the arithmetic mean of the parallel determination results as the determination result. The ratio -- of the absolute difference between the two parallel determination results TO the arithmetic mean -- is not more than 20%.

------ The End ------